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**NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D.C.**



6 June 1952
Report No. 621
(Quarterly) 12
Copy No.

EXPLOSIVES RESEARCH

Contract N7onr-46208

Project

A DIVISION OF

THE GENERAL TIRE & RUBBER COMPANY



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United States Patent Office Secrecy Order

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Report No. 621
(Quarterly Summary)

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EXPLOSIVES RESEARCH

Contract N7omr-46208

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AEROJET ENGINEERING CORPORATION

Azusa, California

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APPENDIX - SPIA Data Sheets

Methylene N,N'-dinitro-N,N'-bis(trinitroethyl carbamate)

bis(2,2-Dinitropropyl) Nitramine

3,2-Dinitro-1,5-pentane-N,N'-dinitro-N,N'-bis(trinitroethyl carbamate)

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CONTRACT FULFILLMENT STATEMENT

This quarterly summary report is submitted in partial
fulfillment of Contract N7onr-46208.

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Report No. 621

I. SUMMARY

A. This quarterly report is submitted under Contract N7onr-46208 and covers the period 1 February 1952 through 30 April 1952.* The objective of the contract is divided into three phases:

1. Synthesis and physical studies of new high-energy nitro compounds as potential explosives.
2. Desensitization of RDX with materials which will not lower its oxygen balance appreciably.
3. Development of bomb and shell casings made of an explosive plastic.

B. The more important results and conclusions of the work reported are presented below:

1. bis(2,2-Dinitropropyl) nitramine has been prepared by the Mannich condensation of 2,2-dinitropropanol and ammonium acetate, followed by post-nitration. This nitramine, prepared independently by the Naval Ordnance Laboratory, is being evaluated as a competitor for Tetryl as a booster explosive.
2. N,3,3,5,5-Pantanitropiperidine has been synthesized by the Mannich condensation of 2,2,4,4-tetranitro-1,5-pentanediol and ammonium acetate, followed by post-nitration. This nitramine, an analog of RDX in which two of the nitramino groups have been replaced by two dinitro methylene groups, has a calculated ballistic-cstar value of 150.5 and a calculated lead-block value of 165.
3. Dimethyl-4,4,6,8,8-pantanitro-6-aza-undecanedioate has been prepared by the Mannich condensation of two mols of methyl 4,4-dinitro-5-hydroxyvalerate with ammonium acetate, followed by post-nitration. This nitramine has been hydrolyzed to the diacid and converted to the corresponding diacid chloride and diisocyanate.
4. 3,3-Dinitro-1,5-pentane dinitramine has been synthesized from 3,3-dinitro-1,5-pentane diamine.
5. 3,3-Dinitro-1,5-pentane-N,N-dinitro-N,N'-bis(trinitroethyl carbamate) was prepared by the addition of two mols of trinitroethanol to 3,3-dinitro-1,5-pentane diisocyanate, followed by post-nitration.

*See also Aerojet Report No. 512 (14 June 1951); No. 536 (11 September 1951); No. 562 (14 December 1951); No. 589 (13 March 1952).

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6. The following compounds were prepared and submitted to the Naval Ordnance Laboratory for evaluation: methylene N,N'-dinitro-N,N'-bis(trinitroethyl carbamate), 3,3-dinitro-1,5-pentane-N,N'-dinitro-N,N'-bis(trinitroethyl carbamate), bis(2,2-dinitropropyl) nitramine, N-nitro-3,3,3-trinitropropyl-2,2,2-trinitroethyl carbamate, 3,3-dinitro-1,5-pentane dinitramine, N,3,3,5,5-pantanitropiperidine, bis(trinitropropyl) urea, and N-nitro-bis(trinitropropyl)urea. The preliminary evaluation and the SPIA data sheets on the first three compounds are recorded.

7. 2,2-Dinitrobutyl acrylate has been polymerized in bulk to give an acetone-soluble polymer with a molecular weight of 100,000; this value is readily changed by the addition of chain-transfer agents.

8. The solution coating of RDX with fractions of poly 2,2-dinitrobutyl acrylate of various molecular weights did not give satisfactory desensitization. The impact stabilities were not improved by modifying the coating with plasticizers. No correlation between the compatibility of the components of the coating mixture and the degree of desensitization was observed.

9. The emulsion polymerization of 2,2-dinitrobutyl acrylate in a closed vessel gave an acetone-soluble polymer. Coating of RDX with this polymer raised the impact stability to a value comparable to that of picric acid or trinitrobenzene.

II. TECHNICAL PROGRESS: SYNTHESIS OF NEW HIGH EXPLOSIVES

A. INTRODUCTION

1. The present explosives program is directed toward the synthesis of new, stable, high-energy polynitro compounds with a preferred oxygen balance on the positive side or very near zero on the negative side.

2. This report deals with the preparation of nitramines, nitrocarbanates, and nitrocureas. The Mannich reaction has proved to be extremely useful in the synthesis of nitramines. Four new potential high explosives have been synthesized.

B. PREPARATION OF NITRAMINES

1. Preparation of bis(2,2-Dinitropropyl) Nitramine

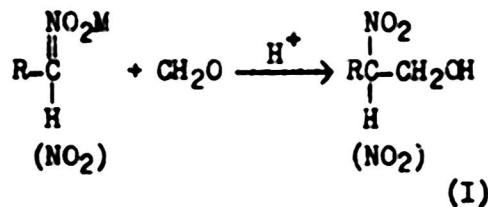
a. Discussion

A study of the Mannich reaction for the preparation of nitramines as potential explosives has been initiated. This is a general reaction which could be applied to any nitro alcohol (I) prepared by the Henry condensation:

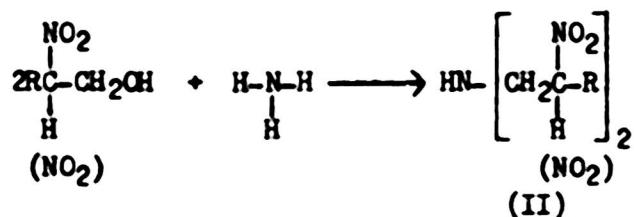
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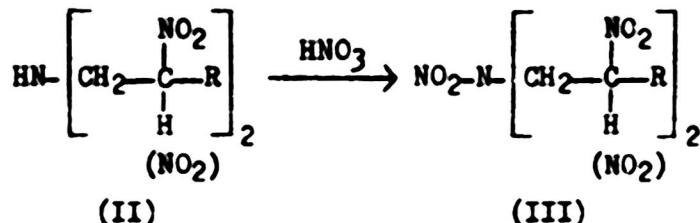
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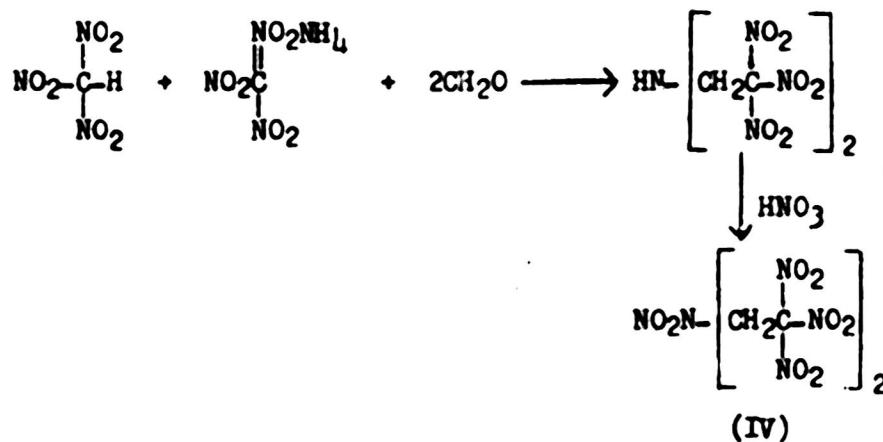
The nitro alcohol (I) could then undergo a Mannich condensation with ammonia or a primary amine. Of most interest to the explosives program were the compounds produced by the condensation of two mols of the nitro alcohol with one mol of ammonia:



This amine (II) could then be nitrated to the corresponding nitramine (III):



The preparation of the high explosive, HMX (IV), by this method is an excellent example of the usefulness of this technique:



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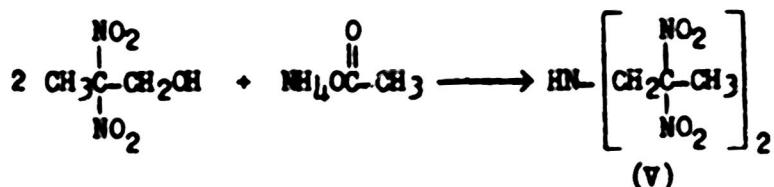
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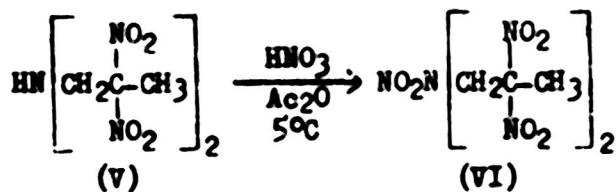
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One of the deficiencies of HOX is its poor thermal stability at higher temperatures. It was believed that the methyl analog of HOX, $\text{NO}_2\text{N}-\left[\begin{array}{c} \text{NO}_2 \\ | \\ \text{CH}_2\text{C}-\text{CH}_3 \\ | \\ \text{NO}_2 \end{array}\right]_2$ (VI),

although poorer in oxygen balance, should exhibit a much higher thermal stability. Thus, with this compound in view, the first reaction studied under the Mannich condensation was that between 2,2-dinitropropanol and ammonia. It was found that by warming an aqueous solution of ammonium acetate with 2,2-dinitropropanol, reaction took place readily, with the formation of bis(2,2-dinitropropyl) amine (V):



This amine (V), a white crystalline solid, mp 62 to 63°C, I.S. >100 cm/2 kg, was readily nitrated with a mixture of acetic anhydride and 100% nitric acid at 5°C to bis(2,2-dinitropropyl) nitramine (VI), a white crystalline compound, mp 187 to 189°C, I.S. = 20 cm/2 kg:



It was later learned that this nitramine had been prepared independently in a similar manner by the Naval Ordnance Laboratory.

b. Experimental

(1) Preparation of bis(2,2-Dinitropropyl) Amine

A solution of 30 g (0.39 mol) of ammonium acetate in 50 ml of water and 30 g (0.20 mol) of 2,2-dinitropropanol was placed in a 125-ml Erlenmeyer flask. The reaction mixture was warmed on the steam bath for 20 min. On cooling, 25.4 g (90.4%) of a cream-colored solid separated; the mp was 55 to 60°C. Recrystallization from methanol and water raised the melting point to 62 to 63°C, I.S. >100 cm/2 kg.

(2) Preparation of bis(2,2-Dinitropropyl) Nitramine

One hundred ml of 100% nitric acid was placed in a 300-ml 3-necked flask, fitted with a mechanical stirrer and thermometer. The flask was cooled in an ice-bath and 100 ml of acetic anhydride was added

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dropwise, while the temperature was maintained at 5 to 10°C. To the solution was added 7.4 g (0.026 mol) of bis(2,2-dinitropropyl) amine. The solution was stirred for 45 min at 5 to 10°C and poured onto ice. The resulting white solid was collected, washed with water, and dried. The yield of bis(2,2-dinitropropyl) nitramine was 7.5 g (87.5%), mp 175 to 180°C. Several recrystallizations from methanol raised the melting point to 187 to 189°C, I.S. = 20 cm²/kg.

Anal. Calc'd for C₆H₁₀N₆O₁₀: %C, 22.09; %H, 3.09; %N, 25.77

Found: %C, 22.52; %H, 3.14; %N, 25.77

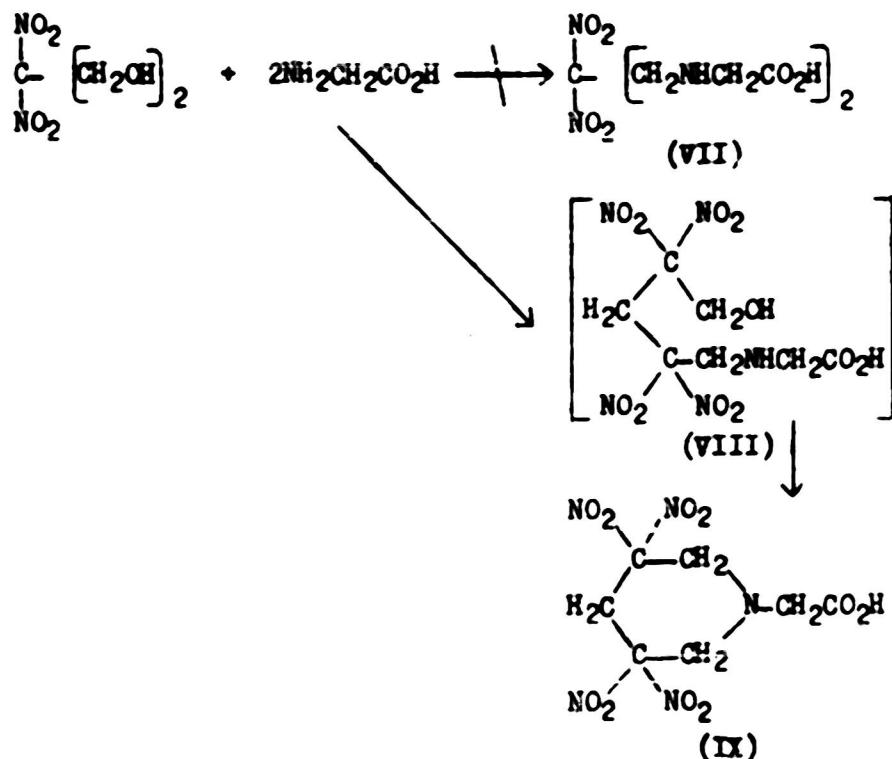
Heat of Combustion, ΔH_p, Predicted: 2600 cal/g

Found: 2597, 2560 cal/g

2. Preparation of N,3,3,5,5-Pantanitropiperidine

a. Discussion

The Mannich reactions of gem dinitro alcohols with glycine and ethanolamine were investigated by Feuer and May* as a means of obtaining nitro monomers which would be useful in the preparation of condensation polymers. Feuer and May reported that the Mannich condensation of 2,2-dinitro-1,3-propanediol with two mols of glycine did not yield the expected 3,7-diaza-5,5-dinitrononanedioic acid (VII), but instead, cyclization occurred and 1-carboxymethyl-3,3,5,5-tetranitropiperidine (IX) was obtained:



*May, Ph.D. Thesis, Purdue University, August 1950.

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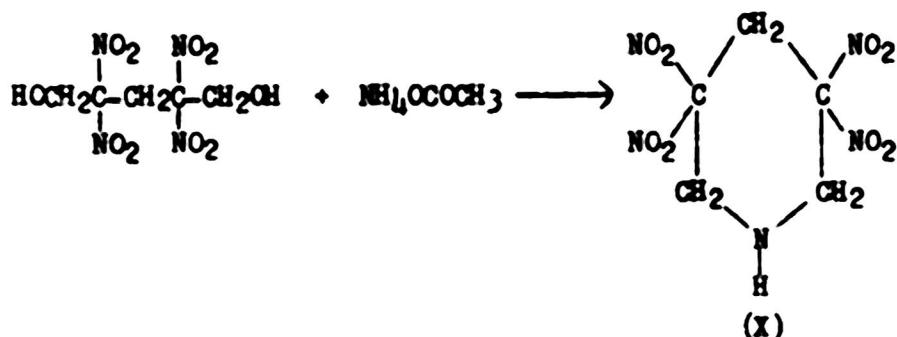
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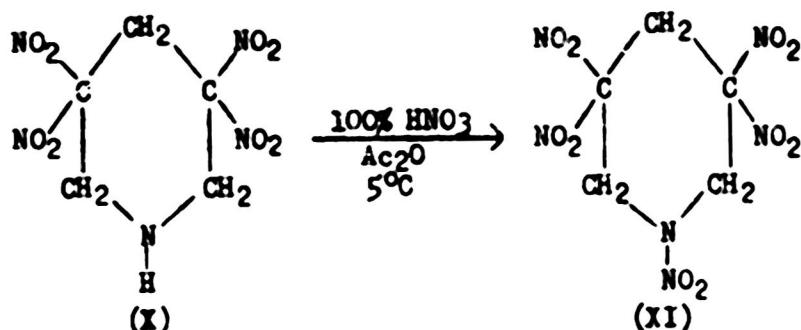
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3-Aza-8-hydroxy-5,5,7,7-tetranitro-octanoic acid (VIII) was postulated as the intermediate in the reaction. The same intermediate would presumably be obtained in the reaction of 2,2,4,4-tetranitro-1,5-pentanediol with glycine, and, as reported earlier,* this proved to be the case. It was of interest in the explosives program to determine whether 2,2,4,4-tetranitro-1,5-pentanediol reacted in a similar manner with ammonium acetate or whether a polynitramine was formed. It was found that the pronounced tendency for the formation of a six-member ring takes precedence over the formation of a linear polymer, resulting in the formation of 3,3,5,5-tetranitropiperidine (IX) from the condensation of 2,2,4,4-tetranitro-1,5-pentanediol and ammonium acetate.



As isolated from the reaction mixture, compound (IX) is an unstable orange solid, mp 108 to 112°C (dec.). Nitration of this crude amine (IX) gave N,3,3,5,5-pentanitropiperidine (XI), a stable white crystalline solid, mp 120 to 125°C (dec.), I.S. = 35 cm²/kg.



Compound (XI) is of interest because it is a carbon analog of RDX in which two nitramino groups have been replaced by two gem dinitromethylene groups. This new nitramine has a calculated ballistic-mortar value of 150.5 and a calculated lead-block value of 165.2.

*Aerojet Report No. 499 (16 March 1951), p. 9; the same piperidine compound (IX) was obtained from this reaction.

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b. Experimental

(1) Preparation of 3,3,5,5-Tetranitropiperidine

A solution of 4 g (0.052 mol) of ammonium acetate in 40 ml of water and 4 g (0.014 mol) of 2,2,4,4-tetranitro-1,5-pentanediol was placed in a 125-ml Erlenmeyer flask. The solution was warmed to 40 to 50°C and after several minutes an orange solid separated. The reaction mixture was cooled and the orange solid was collected and dried to give 2.0 g (53.7%) of 3,3,5,5-tetranitropiperidine, mp 108 to 112°C (dec.).

(2) Preparation of N,3,3,5,5-Pentanitropiperidine

A solution of 8 ml of 100% nitric acid and 8 ml of acetic anhydride was cooled to 5°C, and 0.4 g of 3,3,5,5-tetranitropiperidine was added. The solution was kept at this temperature for 10 min and poured onto ice. The white solid was collected, washed with water, and dried to yield 0.3 g of product, which was recrystallized from chloroform to give white needles, mp 120 to 125°C (dec.), I.S. = 35 cm²/kg.

Anal. Calc'd for C₅H₆N₆O₁₀: %C, 19.36; %H, 1.95; %N, 27.10

Found: %C, 19.65; %H, 1.96; %N, 26.72

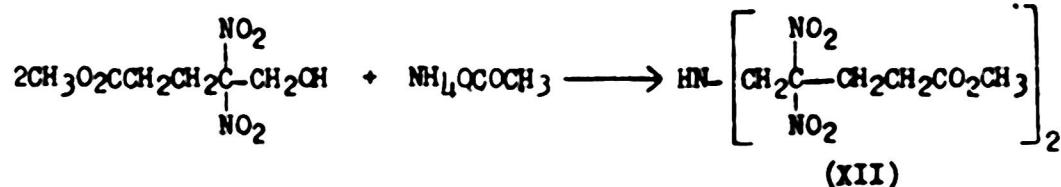
Heat of Combustion, ΔH_p, Predicted: 2075 cal/g

Found: 2085 cal/g
2056 cal/g

3. Preparation of Dimethyl-4,4,8,8-tetranitro-6-aza-undecanedioate

a. Discussion

In extending the scope of the Mannich reaction for the preparation of useful intermediates for the explosives and the nitro polymer programs, it was found that two mols of methyl 4,4-dinitro-5-hydroxyvalerate condensed with ammonium acetate to form dimethyl-4,4,8,8-tetranitro-6-aza-undecanedioate (XII):



The amine is a white crystalline compound, mp 65 to 69°C, I.S. >100 cm²/kg.

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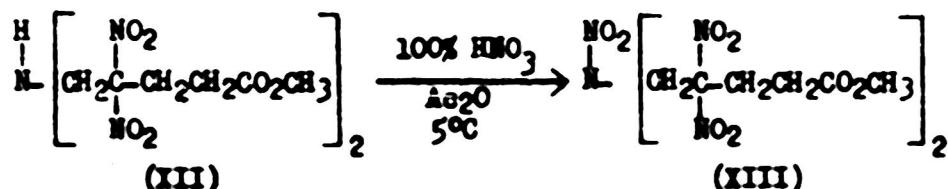
b. Experimental

A solution of 30.0 g (0.39 mol) of ammonium acetate in 75 ml of water and 30.0 g (0.135 mol) of methyl 4,4-dinitro-5-hydroxyvalerate was placed in a 250-ml Erlenmeyer flask. The solution was heated on the steam bath for 10 to 15 min. On cooling, a cream-colored solid separated, which was collected, washed with water, and dried. The yield of dimethyl-4,4,8,8-tetranitro-6-aza-undecanedioate was 25.4 g (88.6%), mp 65 to 69°C, I.S. >100 cm²/kg.

4. Preparation of Dimethyl-4,4,6,8,8-pantanitro-6-aza-undecanedioate

a. Discussion

Dimethyl 4,4,6,8,8-pantanitro-6-aza-undecanedioate (XIII) was prepared by the nitration of dimethyl-4,4,8,8-tetranitro-6-aza-undecanedioate (XII), using a mixture of acetic anhydride and 100% nitric acid:



The nitramine is a white crystalline compound, mp 91 to 92°C, I.S. = 100 cm²/2 kg.

b. Experimental

A nitration mixture of 150 ml of 100% nitric acid and 150 ml of acetic anhydride, cooled to 5 to 10°C, was charged with 25.4 g (0.0598 mol) of dimethyl-4,4,8,8-tetranitro-6-aza-undecanedioate. The solution was stirred for 35 min at 5 to 10°C and poured onto ice. The white solid was collected, washed with water, and dried. The yield of dimethyl-4,4,6,8,8-pantanitro-6-aza-undecanedioate was 17.6 g (62.7%), mp 87 to 89°C, I.S. = 100 cm²/kg. Several recrystallizations from carbon tetrachloride raised the melting point to 91 to 92°C.

Anal. Calc'd for C₁₂H₁₈N₆O₁₄: %C, 30.64; %H, 3.86; %N, 17.87

Found: %C, 30.92; %H, 3.86; %N, 17.94

5. Preparation of 4,4,6,8,8-Pantanitro-6-aza-undecanedioic Acid

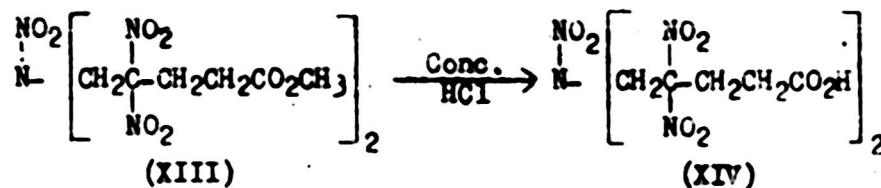
a. Discussion

Dimethyl-4,4,6,8,8-pantanitro-6-aza-undecanedioate (XIII) was readily hydrolyzed with concentrated hydrochloric acid to 4,4,6,8,8-pantanitro-6-aza-undecanedioic acid (XIV), a white crystalline compound, mp 202 to 205°C (dec.).

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b. Experimental

A one-liter Erlenmeyer flask was charged with 85 g (0.18 mol) of dimethyl-4,4,6,8,8-pentanitro-6-aza-undecanedioate and 500 ml of concentrated hydrochloric acid. The mixture was heated on the steam bath for 1.5 hr. The solid was collected, washed with water, and recrystallized from methanol and water to give 50.0 g (30.0%) of 4,4,6,8-pentanitro-6-aza-undecanedioic acid, mp 202 to 205°C(dec.).

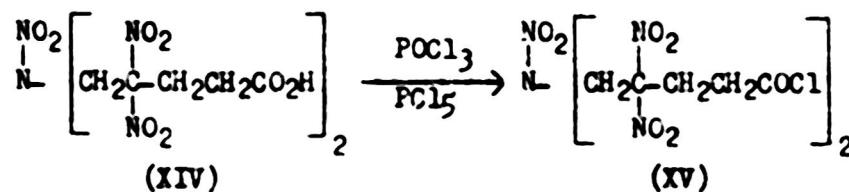
Anal. Calc'd for $C_{10}H_{14}N_6O_4$: %C, 27.16; %H, 3.19; %N, 19.00

Found: C, 27.90; H, 3.32; N, 18.79

6. Preparation of 4,4,6,8,8-Pantanitro-6-aza-undecanoyl Chloride

a. Discussion

4,4,6,8,8-Pentanitro-6-aza-undecanedioic acid (XIV) was converted to the diacid chloride (XV) with a mixture of phosphorous oxychloride and phosphorous pentachloride.



Compound (IV), mp 152 to 155°C (dec.), I.S. = 90 to 100 cm²/2 kg, gave a poor nitrogen and chlorine analysis; another sample will be purified and submitted for analysis. The diacid chloride will be useful in condensation polymerizations.

b. Experimental

A 50-ml Erlenmeyer flask was charged with 3.0 g (0.0068 mol) of 4,4,6,8,8-pentanitro-6-aza-undecanedioic acid and 3 ml of phosphorous oxychloride. Enough phosphorous pentachloride was added to give a solution when the reaction mixture was warmed on the steam bath. The solution was heated on the steam bath for 10 min and benzene was added to

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precipitate 2.0 g (61.4%) of white solid. The product was purified by dissolving in phosphorous oxychloride and reprecipitating with hexane; the mp was 152 to 155°C(dec.), and I.S. = 90 to 100 cm²/kg.

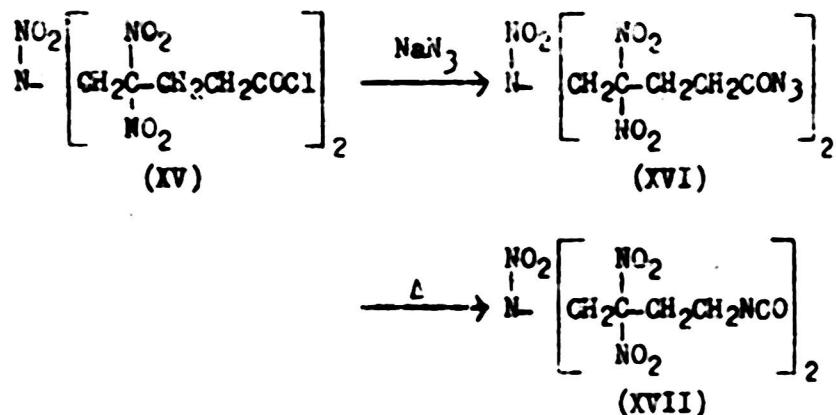
Anal. Calc'd for C₁₀H₁₂N₆O₁₂Cl₂: %C, 25.06; %H, 2.53; %N, 17.54; %Cl, 14.80

Found: %C, 25.43; %H, 3.04; %N, 19.38; %Cl, 13.84

7. Preparation of 3,3,5,7,7-Pantanitro-5-aza-nonane Diisocyanate

a. Discussion:

4,4,6,8,8-Pantanitro-5-aza-undecanedioyl chloride (XV) was converted to the diazide (XVI), which was decomposed to the corresponding diisocyanate (XVII):



The diisocyanate is a white crystalline compound, mp 92 to 95°C(dec.), and will be useful for condensation polymerizations and as an intermediate in the preparation of trinitroethyl carbamates for the explosives program.

b. Experimental

A 500-ml 3-necked flask, fitted with a mechanical stirrer and thermometer, was charged with 12.5 g of crude 4,4,6,8,8-pantanitro-5-aza-undecanedioyl chloride, 150 ml of glacial acetic acid, and 10 g of sodium azide. The reaction mixture was stirred for 1 hr at 15 to 20°C; no heat of reaction was evident. Methylene chloride, 150 ml, was added and the mixture was washed with water, 1% sodium bicarbonate, and water. The methylene chloride solution was dried and concentrated in vacuo to give a white solid, mp 80 to 90°C(dec.). Dry chloroform was added to the solid and the solution was refluxed for 2 hr, with the evolution of 0.5 liter of nitrogen gas. The solution was concentrated

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II Technical Progress, B (cont.)

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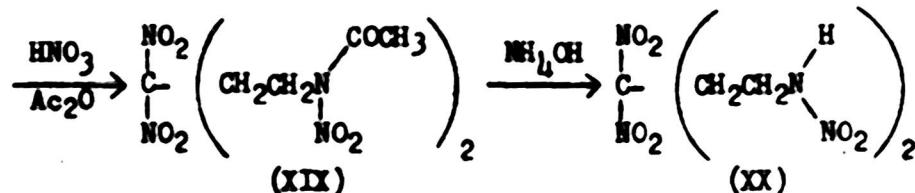
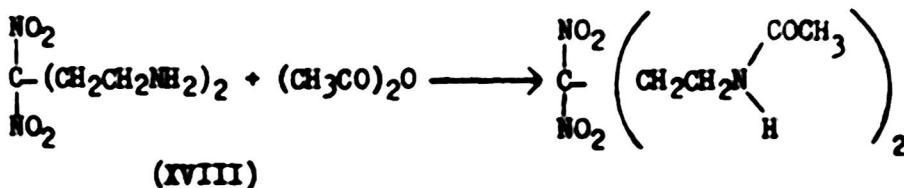
in vacuo, leaving a brown solid. The product was dissolved in dioxan and reprecipitated with carbon tetrachloride. Recrystallization from chloroform gave a white crystalline solid, mp 92 to 95°C(dec.).

Anal. Calc'd for $C_{10}H_{12}N_8O_{12}$: %C, 27.53; %H, 2.77; %N, 25.69
Found: %C, 28.83; %H, 3.22; %N, 25.71

8. Preparation of 3,3-Dinitro-1,5-pentane Dinitramine

a. Discussion

The great contribution of the nitramino group to the explosive power of a compound is well illustrated in compounds such as methylene dinitramine and ethylene dinitramine. It was of interest to prepare similar dinitramino compounds containing additional nitro groups, and to determine the physical properties and explosive power of such compounds. Accordingly, 3,3-dinitro-1,5-pentane dinitramine was prepared according to the following equations:



3,3-Dinitro-1,5-pentane diamine was acetylated and nitrated to 3,3-dinitro-N,N'-dinitro-N,N'-diacetyl-1,5-pentanediamine (XIX). Compound (XIX) was very readily hydrolyzed with ammonium hydroxide to give 3,3-dinitro-1,5-pentane dinitramine, a white crystalline compound with the surprisingly low melting point of 67 to 68°C, I.S. = 30 to 35 cm²/kg, calculated ballistic-mortar value = 142, and the calculated lead-block value = 132.

b. Experimental

(1) Preparation of 3,3-Dinitro-N,N'-diacetyl-1,5-pentanediamine

Two hundred ml of acetic anhydride was slowly added to a solution of 121.7 g (0.63 mol) of 3,3-dinitro-1,5-pentanediamine in 250 ml of dry benzene. The reaction mixture was warmed on the steam bath,

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II Technical Progress, B (cont.)

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cooled, and filtered. The solid was triturated with warm water, cooled, and filtered, to give 110 g (62.8%) of N,N'-diacetyl-3,3-dinitro-1,5-pentanediamine, mp 157 to 159°C.

(2) Preparation of 3,3-Dinitro-N,N'-dinitro-N,N'-diacetyl-1,5-pentanediamine

A nitration mixture of 250 ml of 100% nitric acid and 250 ml of acetic anhydride was cooled to 5°C and 96.4 g (0.36 mol) of 3,3-dinitro-N,N'-diacetyl-1,5-pentanediamine was added. The solution was stirred for 40 min and poured onto ice. The cream-colored solid was collected, washed with water, dried, and recrystallized from chloroform to give 65.2 g (50%) of 3,3-dinitro-N,N'-dinitro-N,N'-diacetyl-1,5-pentanediamine, mp 93 to 96°C, I.S. >100 cm²/kg. Two additional recrystallizations from chloroform raised the melting point to 100 to 101°C.

Anal. Calc'd for C₉H₁₄N₆O₁₀: %C, 29.51; %H, 3.85; %N, 22.95

Found: %C, 29.84; %H, 3.83; %N, 23.67

(3) Preparation of 3,3-Dinitro-1,5-pentane Dinitramine

Twenty-five ml of 28% ammonium hydroxide was added to 10.0 g (0.0027 mol) of 3,3-dinitro-N,N'-dinitro-N,N'-diacetyl-1,5-pentanediamine. The solid immediately dissolved with the evolution of heat to form a yellow solution. The solution was cooled and acidified with concentrated hydrochloric acid, causing a yellow oil to separate. The reaction mixture was extracted twice with ether; the ether extracts were combined, washed twice with water, dried, and concentrated to give a yellow oil. Addition of chloroform caused the oil to crystallize to a white solid. The product was collected and washed with methylene chloride. The yield of 3,3-dinitro-1,5-pentane dinitramine was 5.5 g (71.3%), mp 62 to 65°C. Two recrystallizations from anhydrous ether raised the melting point to 67 to 68°C, I.S. = 30 to 35 cm²/kg.

Anal. Calc'd for C₅H₁₀N₆O₈: %C, 21.28; %H, 3.57; %N, 29.79

Found: %C, 21.40; %H, 3.72; %N, 30.43

Heat of Combustion, ΔH_p, Predicted: 2725 cal/g

Found: 2681 cal/g

C. PREPARATION OF NITRO CARBAMATES

1. Preparation of 3,3-Dinitro-1,5-pentane-bis(trinitroethyl carbamate)

a. Discussion

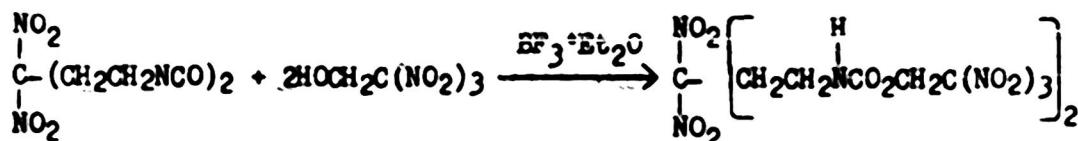
Work on the preparation of nitro carbamates as potential explosives has been continued. It has been found that two mols of trinitroethanol

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II Technical Progress, C (cont.)

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will add to 3,3-dinitro-1,5-pentane diisocyanate in the presence of boron trifluoride etherate, to give 3,3-dinitro-1,5-pentane-bis(trinitroethyl carbamate), a white crystalline solid, mp 96 to 97°C, with an impact stability of 35 cm/2 kg.



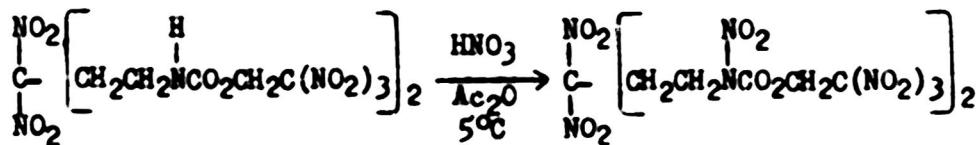
b. Experimental

A one-liter round-bottom flask fitted with a condenser and drying tube was charged with 48.8 g (0.2 mol) of 3,3-dinitro-1,5-pentane diisocyanate, 72.4 g (0.4 mol) of trinitroethanol, 400 ml of dry alcohol-free chloroform, and 52 ml (0.4 mol) of boron trifluoride etherate. The solution was refluxed for 24 hr, cooled, and washed with four 250-ml portions of water. During the final water-washing a cream-colored solid separated from the chloroform solution. The product was collected, washed with chloroform, and dried to give 75 g (61.8%) of 3,3-dinitro-1,5-pentane-bis(trinitroethyl carbamate), mp 96 to 97°C, I.S. = 35 cm/2 kg.

2. Preparation of 3,3-Dinitro-1,5-pentane-N,N'-dinitro-N,N''-bis(trinitroethyl carbamate)

a. Discussion

The nitration of 3,3-dinitro-1,5-pentane-bis(trinitroethyl carbamate) with a mixture of 100% nitric acid and acetic anhydride at 5°C gave 3,3-dinitro-1,5-pentane-N,N'-dinitro-bis(trinitroethyl carbamate). The product is a white crystalline compound, mp 151 to 152°C, I.S. = 25 to 30 cm/2 kg, oxygen balance = -9.2, ballistic mortar value = 140, and lead-block value = 165.



b. Experimental

A nitration mixture of 50 ml of 100% nitric acid and 50 ml of acetic anhydride was cooled in an ice bath and 5.0 g of 3,3-dinitro-1,5-pentane-bis(trinitroethyl carbamate) was added. The reaction mixture was stirred for 20 min and poured onto ice. The white solid was collected, washed with water, and dried to give 4.9 g of product, mp 148 to 150°C. T_m

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recrystallizations from methylene chloride raised the melting point to 151 to 152°C, I.S. = 25 to 30 cm²/kg.

Anal. Calc'd for C₁₁H₁₂N₂O₂4: %C, 18.97; %H, 1.74; %N, 24.14
Found: %C, 19.19; %H, 1.77; %N, 23.87

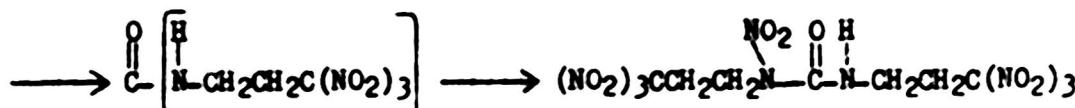
Heat of Combustion, ΔH_p Predicted: 1784 cal/g
Found: 1776 cal/g

D. PREPARATION OF NITRO UREAS

1. Preparation of bis(Trinitropropyl) Urea

a. Discussion

During the past quarter additional quantities of bis(trinitropropyl) urea and N-nitro-bis(trinitropropyl) urea* were prepared for evaluation by the Naval Ordnance Laboratory. The starting material for these syntheses was 4,4,4-trinitrobutyryl chloride:



3,3,3-Trinitropropyl isocyanate is a light-yellow liquid. However, in some of the preparations a high-melting solid was obtained instead of this liquid. This solid was thought to be the cyclic dimer or trimer of 3,3,3-trinitropropyl isocyanate.** It has now been shown that this high-melting solid is actually the bis(trinitropropyl) urea formed as a result of incomplete drying of the azide solution prior to decomposition to the corresponding isocyanate.

b. Experimental

The solid formed in the preparation of 3,3,3-trinitropropyl isocyanate was recrystallized from chloroform to give white needles, mp 170 to 171°C(dec.).

Anal. Calc'd for C₇H₁₀N₈O₁₃: %C, 20.30; %H, 2.43; %N, 27.05

Found: %C, 20.44; %H, 2.35; %N, 27.04

Heat of Combustion, ΔH_p Predicted: 2198 cal/g

Found: 2164 cal/g

*Aerojet Report No. 589 (13 March 1952), p. 10.

**Aerojet Report No. 562 (14 December 1951), p. 12.

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E. PREPARATION OF SAMPLES FOR EVALUATION BY THE NAVAL ORDNANCE LABORATORY

1. The following samples were prepared and submitted to Naval Ordnance Laboratory for evaluation:

a. Methylene N,N'-dinitro-bis(trinitroethyl carbamate), 22.5 g, mp 112 to 113°C, I.S. = 25 to 30 cm²/kg.

b. 3,3-Dinitro-1,5-pentane-N,N'-dinitro-N,N'-bis(trinitroethyl carbamate), 18.6 g, mp 151 to 152°C, I.S. = 25 to 30 cm²/kg.

c. N-Nitro-3,3,3-trinitropropyl-2,2,2-trinitroethyl carbamate, 13.6 g, mp 96 to 97°C, I.S. = 30 cm²/kg.

d. bis(2,2-Dinitropropyl) nitramine, 21.2 g, mp 187 to 189°C, I.S. = 20 cm²/kg.

e. 3,3-Dinitro-1,5-pentane dinitramine, 3 g, mp 65 to 66°C, I.S. = 30 to 35 cm²/kg.

f. N,3,3,5,5-Pantanitropiperidine, 5 g, mp 119 to 124°C (dec.), I.S. = 35 cm²/kg.

g. bis(Trinitropropyl) urea, 5 g, mp 167 to 169°C (dec.), I.S. = 60 to 65 cm²/kg.

h. N-Nitro-bis(trinitropropyl) urea, 5 g, mp 79 to 81°C (dec.), I.S. = 30 to 35 cm²/kg.

2. The conclusions reached by the Naval Ordnance Laboratory with respect to three of these compounds are as follows:

a. Methylene N,N'-Dinitro-N,N'-bis(trinitroethyl carbamate)

This compound is of interest because of its high density, good thermal stability, and surplus of available oxygen. On the other hand, it would require extensive desensitization for pressed-charge applications, and could probably never be cast alone or in mixtures in which it is dissolved when melted. The compound is unstable above its melting point or when dissolved in liquid TNETB at 100°C. Its compatibility with waxes at elevated temperatures is being determined.

b. 3,3-Dinitro-1,5-pentane-N,N'-dinitro-N,N'-bis(trinitroethyl carbamate)

Although this compound is thermally stable, the density is not high enough, and the impact sensitivity is greater than that of PETN. It is, therefore, of no interest at the present time.

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II Technical Progress, E (cont.)

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c. bis(2,2-Dinitropropyl) Nitramine

Additional tests have been performed on this compound, prepared both at NCL and Aerojet. It is being evaluated as a competitor for Tetryl as a booster explosive. The tests reported in Table I were designed to follow the decomposition rate at elevated temperature. Tetryl decomposes rapidly above its melting point (130°C). The stability shown for the nitramine is remarkably good.

F. THE ESTIMATION OF EXPLOSIVE POWER OF HIGH EXPLOSIVES

A simple method for the estimation of the explosive power of high explosives has been formulated at Aerojet.* Recently, it has come to our attention that similar work has been performed by Handrick at the Arthur D. Little Co.** Handrick calculated the force (the product nRT) for explosives by using a value for the explosion temperature T which was obtained by a process of iteration rather than by an approximation; in this way the power of an explosive was calculated to be 100 times the ratio of its force to that of TNT. Close agreement was found in nearly all cases between this power and the power observed in the ballistic mortar. These calculations confirm the validity of the correlation between ballistic mortar value and force found at Aerojet. For the survey purposes to which the correlation is being applied, the approximate methods developed at Aerojet are sufficiently accurate.

III. POLY 2,2-DINITROBUTYL ACRYLATE

A. INTRODUCTION

The previous quarterly report**** described the polymerization of 2,2-dinitrobutyl acrylate for use in the coating of RDX from emulsion and solution. The nitro monomer was polymerized in emulsion and in bulk, giving an insoluble polymer. When RDX was coated with this nitro polymer the results were unsatisfactory and unreproducible. Impurities in the monomer probably caused cross-linking, which would result in an insoluble polymer. This problem was investigated, and the 2,2-dinitrobutyl acrylate was successfully purified.**** Bulk polymerization of this new and pure monomer gave a high-molecular-weight polymer which was acetone-soluble. It was desirable to determine the molecular weight of this nitro polymer and to ascertain the influence of polymerization additives on molecular weight in order to determine the effect of coating RDX from solution with representative polydinitrobutyl acrylates of various molecular weights.

*Aerojet Report No. 512, p. 8.

**G. R. Handrick, "Calculation of Power" in Arthur D. Little, Inc. Report "Fundamental Research on High Explosives," Abstract of Work Performed Under Contract DA-19-020-ORD-12, July 1949 through October 1950, p. 27.

***Aerojet Report No. 589, p. 14.

****Aerojet Report No. 590, p. 52.

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TABLE I
NOT PRELIMINARY TESTS ON EXPERIMENTAL EXPLOSIVES

Recreationalized art NOL

Tetryl (for comparison with
A52-3)

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III Poly 2,2-Dinitrobutyl Acrylate (cont.)

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B. DETERMINATION OF MOLECULAR WEIGHT

1. Standardization of Viscometric Molecular Weights

a. The determination of the intrinsic viscosity of a polymer from its relative viscosity at various concentrations affords a speedy method for the determination of molecular weight. However, the method is not absolute; its use with any polymer depends on standardization with fractions of known molecular weights. This standardization gives the constants of the Staudinger equation, which relates intrinsic viscosity to molecular weight. Absolute values of molecular weight can be determined by osmotic pressure measurements.

b. For purposes of standardization, several specimens of polymer were made in a bulk process, using different chain-transfer additives and different conditions to give a variety of molecular weights. These preparations are described in Table II.

c. Intrinsic viscosities of these materials were determined, as shown in Table II. For the first three, viscosities were measured in acetone solutions at several concentrations, and intrinsic viscosities were derived by extrapolation; for specimen d1 a measurement at only one concentration was made, and the intrinsic viscosity was calculated from this measurement by use of the Baker equation. (This equation had previously been shown to hold accurately for polydinitrobutyl acrylates.)

d. Concurrently, osmotic pressures were measured with Zimm-Myerson osmometers. Molecular weights were determined at different concentrations in acetone from the equation $nV = NRT$, with the intention of extrapolating to zero concentration, at which this ideal relation is valid. However, the calculated molecular weights showed no trend with concentration; accordingly, they were simply averaged for each polymer. Molecular weights, for specimens a and b were obtained in this manner, as shown in Table II. In spite of much effort, tests on specimens c and d1 have so far given very erratic results. However, this work is being continued, with the aim of providing corresponding values of intrinsic viscosity and molecular weight for a sufficient number of fractions to establish firmly the constants of the Staudinger equation.

2. The Influence of Polymerization Additives on Molecular Weight

a. To test the effects of various catalysts, retarders, and chain-transfer agents on dinitrobutyl acrylate polymerization, and to ascertain what range of molecular weights can be attained, a series of samples was prepared for bulk polymerization. Each sample contained 5 g of a standard dinitrobutyl acrylate. In the various formulations, other free-radical catalysts were substituted for MAKP, or this catalyst was supplemented with chain-transfer agents and retarders (tertiary dodecyl mercaptan, carbon tetrachloride, and 2,2-dinitropropane). All samples were cured on the same schedule. The appearance of the reaction products is described in Table III.

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III Poly 2,2-Dinitrobutyl Acrylate, B (cont.)

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TABLE II
 PREPARATION OF POLY 2,2-DINITROBUTYL ACRYLATE AND
 RELATION OF INTRINSIC VISCOSITIES TO MOLECULAR WEIGHTS
 (All measurements made on acetone solutions at 25°C)

<u>Specimen</u>	<u>Additives, UNBA Basis</u>	<u>Cure</u>	<u>Preparation</u>
a	1.0% MAKP + 1.0% dodecyl mercaptan	5 days at 45°C 2 days at 60°C	(1) 10 g dissolved in 50 ml acetone Precipitated from 500 ml methanol (2) Dissolved in 25 ml acetone Precipitated from 500 ml methanol
b	1.0% MAKP + 57% CCl_4	2 days at 60°C	3 times: 10 g dissolved in 25 ml acetone Precipitated from 500 ml methanol
c	1.0% MAKP	2 days at 60°C	3 times: 10 g dissolved in 25 ml acetone Precipitated from 500 ml methanol
d1	1.0% MAKP	3 days at 45°C 2-3/4 days at 60°C 1 day at 85°C	(1) 14.4 g dissolved in 500 ml acetone Precipitated from 750 ml methanol (2) Ppt. (1) dissolved in 500 ml acetone Precipitated from 700 ml methanol (4.6 g yield)

<u>Specimen</u>	<u>Conc. 100 ml</u>	<u>η_r</u>	<u>[η]</u>	<u>Osmometer</u>	<u>Conc. 100 ml</u>	<u>M</u>	<u>Average M</u>
a	1.000	1.417	0.365	A	1.442	57,000	
	0.600	1.238		C		63,000	62,000
	0.200	1.075		A	0.834	65,000	
b	1.000	1.656	0.535	A	1.620	78,000	
	0.600	1.366		C		74,000	79,000
	0.200	1.111		A	1.108	82,000	
c	1.000	1.908	0.720				
	0.600	1.500		C		83,000	
	0.203	1.154		A	0.618	77,000	
d1	1.000	2.305	0.88*				

*Calculated from Baker equation: $[\eta] = \frac{8}{c} (\eta_r^{0.125} - 1)$

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III Poly 2,2-Dinitrobutyl Acrylate, B (cont.)

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TABLE III

COMPARISON OF PRODUCTS FROM 2,2-DINITROBUTYL ACRYLATE POLYMERIZATIONS
 (Curing Schedule: 3 days at 45°C, 2-3/4 days at 60°C, 1 day at 85°C)

<u>Formulation of Other Components, on Basis of 5.0 g DNBA</u>	<u>Description of Reaction Product</u>	<u>Reprecipitated Polymer [η]</u>
1.025 CCl ₄ + 15 MAKP (based on DNBA)	Soft, rubbery; amber-colored; few bubbles	0.529
5.0 g CCl ₄ + 15 MAKP	Flexible; flows; transparent; foamy*	0.362
10.0 g CCl ₄ + 15 MAKP	Thick fluid; transparent; bubbles all escaped	0.276
15 Azo bis methyl isobutyrate	Tough, slightly flexible; transparent; bubbly	0.644
15 Azo bis isobutyronitrile	Brittle; light amber; bubbly	0.620
5.25 MAKP	Tough, slightly flexible; dark amber; bubbly	0.198
0.113 Tert. dodecyl mercaptan + 15 MAKP	Tough, slightly flexible; light amber; bubbly	0.505
0.328 Tert. dodecyl mercaptan + 15 MAKP	Tough, slightly flexible; amber; no bubbles	0.275
1.002 Tert. dodecyl mercaptan + 15 MAKP	Thick fluid; light amber; few small bubbles	0.230
5% Dinitropropane + 15 MAKP	Tough, slightly flexible; light amber; bubbly	0.576
15 MAKP	Tough, slightly flexible; light amber; bubbly	0.598

* Gel phase from reaction mixture.

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III Poly 2,2-Dinitrobutyl Acrylate, B (cont.)

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b. Low-molecular-weight fractions were eliminated from each product by dissolving 2.5 g (or one-half of the gel phase) in 12 ml of acetone, and reprecipitating the polymer from 360 ml of methanol while stirring it rapidly in a Waring Blender. Intrinsic viscosities of the dried, reprecipitated polymers were determined; these results are also given in Table II.

c. Differences of activity of the various catalysts are reflected in the differences of molecular weight. Also, as would be predicted, an increase in MAKP catalyst from 1 to 5.2% causes an appreciable lowering of the molecular weight of the product. Carbon tetrachloride, mercaptan, and dinitropropane all lower the molecular weight, as expected, and the effect increases with increasing amounts. The range of values of intrinsic viscosity suggests the possibility of fixing the molecular weight anywhere within a wide range by a suitable combination of additives.

IV. DESENSITIZATION OF RDX

A. BY COATING FROM SOLUTION WITH POLY 2,2-DINITROBUTYL ACRYLATE AND POLYMER I-A

1. Discussion

a. In desensitizing RDX by applying a coating from solution, previous work had shown the need of a more effective coating and of reducing the amount of surface-active agent used (4% of the RDX, in the best preparations hitherto). Polydinitrobutyl acrylate seemed to hold promise as a coating material applied in this way. Accordingly, a polymer of about 100,000 molecular weight was tested in the process, using those surface-active agents which previous experience had shown to be best. However, even with 4% of agent, the amount of desensitization achieved with 5% of polymer was small.

b. On this basis, two procedures were adopted. First, the introduction of plasticizers into the coating was investigated. Second, the application of polymers of different molecular weights was studied, in the hope that the physical properties of a polymer of another molecular weight would provide superior desensitization.

c. Some compatibility tests were performed for guidance in the choice of plasticizers. It is not known how compatibility is related to effectiveness in desensitizing explosives. The results show that the plasticizer which forms the most flexible compatible film with the polymer, dioctyl sebacate, does not necessarily give the best desensitization (cf. results for dinitropropane). Since most of the surface-active agent has been shown to be retained on the RDX surface, possibly the ternary system of polymer-plasticizer-agent should be considered. A number of experiments were performed with dinitropropane as a plasticizer, in an effort to obtain a compatible film of fair mechanical properties. Such a film was obtained with the formulation of polymer/DNP/glyceryl monoleate, 5/4/2, but the desensitization achieved with a coating of this composition was mediocre.

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IV Desensitization of RDX, A (cont.)

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d. In this connection it was also noted that the efficacy of plasticizers appears to depend on the surface-active agents used. Thus, dinitropropane appears to be better than Emery dimer acids with Span 85, but worse with Prosol 307.

e. On the whole, no clear relation between compatibility and desensitization has been demonstrated by these few results and none of the results seem good enough to justify the further work needed to establish positively the presence or absence of a relation, inasmuch as all values of impact stability were well below 100 cm/2 kg.

f. Representative polydinitrobutyl acrylates of various molecular weights were tested as coating materials. Impact stabilities of all the products were poor, even though 10% polymer was used. In the same formulations, polymer I-A gave distinctly better desensitization.

2. Experimental

a. A sample of pure dinitrobutyl acrylate was polymerized in bulk using 1% MAKP catalyst, and cured according to the following schedule:

3 days at 45°C
2-3/4 days at 60°C
1 day at 85°C

The resulting polymer, a tough, amber-colored mass including some bubbles, was dissolved in several volumes of acetone. The polymer was reprecipitated by slowly adding 1 volume of solution to 30 volumes of methanol, stirred rapidly in a Waring Blender, and the solvent was dried under vacuum.

b. Viscosity measurements led to a value of intrinsic viscosity, $[\eta]$, of 0.592, and the osmometric molecular weight was approximately 100,000.

c. This polymer was used for coating RDX, with the results shown in Table IV. All impact stabilities reported here apply only to the "original" material (a friable crust or small globules) which resulted from the drying operation.

d. The first tabulated values are for the polymer alone (5% of RDX), using various amounts of Span 85 as surface-active agent. A single test of the compatibility of polymer and Span 85 is also described.

e. The latter part of the table shows the results of attempts to improve the coating with various plasticizers. (Also included are a few data on the plasticization of polymer I-A.) With three of these materials, dioctyl sebacate, dinitropropane, and Emery dimer acids, tests were performed for both compatibility and desensitization.

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Figure 2-1 is a picture of a 3-dimensional, 3-dimensional, 3-dimensional diagram.

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V Desensitization of RDX, A (cont.)

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f. The effect of adding a small amount of methocel (methyl cellulose) was tested. This compound is used at the Naval Ordnance Test Station, Inyokern, as a dispersing agent. Comparison of the results with those obtained for the same formulations without methocel shows that the improvement is negligible:

<u>Slurry Medium, per 1.00 g RDX</u>	<u>Coating Sol'n</u>	<u>I.3. cm/2 kg</u>
15 ml water + 5 ml acetone + 0.010 g Span 85 + 0.005 g methocel	0.050 g Poly DNBA in 2 ml EtOAc	35 to 40
15 ml water + 5 ml acetone + 0.010 g Span 85 + 0.005 g methocel	0.050 g I-A in 2 ml EtOAc	40 to 45

g. To test the relation of the molecular weight of poly-dinitrobutyl acrylate to effectiveness in desensitization, different preparations, including an emulsion polymerization product and several of the bulk polymers described in Table II, were applied as coatings. To compensate for the reduced amount of surface-active agent used, 10% of polymer (based on RDX) was taken in each case. The results, given in Table V, show that none of the polydinitrobutyl acrylates are particularly effective in desensitization. A few applications of polymer I-A in similar formulations show this polymer to be distinctly better.

B. BY COATING FROM EMULSION WITH POLY 2,2-DINITROBUTYL ACRYLATE

1. Emulsion Polymerization of 2,2-Dinitrobutyl Acrylate

a. Discussion

(1) The emulsion polymerization of the new, pure 2,2-dinitrobutyl acrylate was studied using the same type of recipes that were employed in the previous work. The polymerizations were first carried out on a small scale in test tubes and screw-top bottles which were rotated end over end in a water bath at 45°C. When 5% Nonisol 210 was used as the emulsifying agent and 0.2% MAKP as the catalyst, the polymerization took place very slowly and in poor yield (36 to 46%), but the polymer that was obtained was acetone-soluble.

(2) In order to conduct the work on a larger scale, the remaining emulsion polymerizations were carried out in a three-necked flask. The flask was fitted with a mechanical stirrer and the polymerization was run in a nitrogen atmosphere. However, the results obtained in this type of vessel were entirely different from those obtained using the apparatus described in Paragraph (1), above. In all cases the nitro polymer obtained was acetone-insoluble; the reason for this is not yet apparent. Further studies will be

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V Desensitization of RDX, B (cont.)

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TABLE V

**EFFECT OF MOLECULAR WEIGHT OF POLY 2,2-DINITROBUTYL ACRYLATE
ON RDX DESENSITIZATION**

(In all preparations, slurry consists of 1.00 g RDX in 15 ml water + 5 ml acetone + surface-active agent; coating solution contains 0.10 g polymer in 2 ml ethyl acetate)

<u>Surface-Active Agent</u>	<u>Polymer</u>	<u>Impact Stability cm/2 kg</u>
0.040 g Span 85	Emulsion Poly DNBA	30 to 35
0.040 g Span 85	Emulsion Poly DNBA (coating temp. = 60°C)	55 to 60
0.010 g Span 85	Emulsion Poly DNBA	45 to 50
0.010 g Span 85	Emulsion Poly DNBA (coating temp. = 60°C)	35 to 40
0.010 g glycaryl mono oleate	Poly DNBA, $[\eta] = 0.230$	55 to 60
0.010 g glycaryl mono oleate	Poly DNBA, $[\eta] = 0.362$	35 to 40
0.010 g glycaryl mono oleate	Poly DNBA, $[\eta] = 0.498$	35 to 40
0.010 g glycaryl mono oleate	Poly DNBA, $[\eta] = 0.598$	55 to 60
0.010 g glycaryl mono oleate	Poly DNBA (not reprecipitated)*	40 to 45
0.010 g Span 85	L-A	65 to 70
0.010 g glycaryl mono oleate	L-A	40 to 45
0.010 g Prosol 307	L-A	60 to 65

* $[\eta] = 0.275$ after reprecipitation.

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V Desensitization of RDX, B (cont.)

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made to prepare a soluble polymer. The preparation of Nonisol 210 and MAKP in the flask was not satisfactory, as poor emulsions were obtained. When 7.5% Tween 40 and 1% $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were used at 45°C, good emulsions containing 68.1% polymer (N-261) were obtained in 48 hr. The addition of additives such as 2,2-dinitropropane, lecithin, and CR-39 (cross-linking agent) caused a decrease in the rate of polymerisation.

b. Experimental

The experimental results are summarized in Table VI.

2. Coating of RDX

a. Discussion

In the coating of RDX with the emulsion of poly 2,2-dinitrobutyl acrylate, three significant factors emerged:

(1) The coated samples of RDX with the highest impact stability were obtained from the emulsion containing the acetone-soluble polymer (N-252-I and N-252-J).

(2) It was found that it was not necessary in many cases to add methanol to precipitate the polymer from the emulsion onto the RDX. Apparently, the mere mixing of the aqueous slurry of RDX, Span 85, and the emulsion, causes the polymer to precipitate from the emulsion onto the RDX.

(3) It was shown that RDX could be coated with less than the 2.5% Span 85 which has normally been employed. Thus, using 5% 2,2-dinitrobutyl acrylate and 0.5 to 2.5% Span 85, coated samples of RDX were obtained which had an impact stability of >100 cm²/kg (RDX = 34). In order to bring these values down to a measurable range, the determinations of impact stabilities were repeated by placing the samples on 5/0 sand paper. The coated RDX samples then had an impact stability of about 30 to 35 cm²/kg as compared with RDX = 28, picric acid = 35, trinitrobensene = 30 to 35, TNT = 67, and composition A = 50 to 55. The samples were pressed at 15,000 psi and the impact stabilities were lowered, from >100, to 70 to 100 cm²/kg. The RDX coated with the insoluble nitro polymer gave low impact stabilities, from 30 to 100 cm²/kg. The addition of 1% of plasticizers such as 2,2-dinitropropane, dioctyl sebacate, and Emery dimer acids during the coating process did not serve to increase the impact stability.

b. Experimental

(1) Precipitation Using Solvent

Approximately 100 ml of water was placed in a 500-ml resin pot, fitted with a mechanical stirrer, and the 2,2-dinitrobutyl acrylate emulsion was weighed into the pot by difference. Knowing the

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V Desensitization of RDX, B (cont.)

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concentration of the emulsion, the amount of 2,2-dinitrobutyl acrylate that had been dried could then be calculated. The Span 85 was weighed into the pot by difference, stirring was started, and the calculated amount of RDX was added through a powder funnel. The slurry was stirred for 10 min and an equal volume of methanol was added. The mixture was stirred for an additional two minutes and filtered. The coated RDX was washed with methanol and dried in vacuo.

(2) Solvent Precipitation Without the Use of Solvent

This procedure was identical with that described above, except that no methanol was added to the reaction mixture. The coated RDX was washed with water and dried in vacuo over potassium hydroxide for 24 hr. The experimental results are summarized in Table VII.

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TABLE VII
DESENSITIZATION OF RDX WITH POLY 2,2-DINITROETHYL ACRYLATE

Sample (a) No.	Emulsion Pct.	RDX %	Water %	Wetting Agent %	Plasticizer %	I.D. (in/2 in.)		Pressed to 15,000 psi Without Solvent
						Water (b) %	Wax (c) %	
S-71	S-250	20.6				50	50	
S-72	S-251	21.3				50	50	
S-73	S-252	20.8				50	50	
S-74	S-253	20.9				50	50	
S-75	S-254	21.1				50	50	
S-76	S-255	21.3				50	50	
S-77	S-256	21.5				50	50	
S-78	S-257	21.5				50	50	
S-79	S-258	21.5				50	50	
S-80	S-259	21.5				50	50	
S-81	S-260	21.5				50	50	
S-82	S-261	21.5				50	50	
S-83	S-262	21.5				50	50	
S-84	S-263	21.5				50	50	
S-85	S-264	21.5				50	50	
S-86	S-265	21.5				50	50	
S-87	S-266	21.5				50	50	
S-88	S-267	21.5				50	50	
S-89	S-268	21.5				50	50	
S-90	S-269	21.5				50	50	
S-91	S-270	21.5				50	50	
S-92	S-271	21.5				50	50	
S-93	S-272	21.5				50	50	
S-94	S-273	21.5				50	50	
S-95	S-274	21.5				50	50	
S-96	S-275	21.5				50	50	
S-97	S-276	21.5				50	50	
S-98	S-277	21.5				50	50	
S-99	S-278	21.5				50	50	
S-100	S-279	21.5				50	50	
S-101 (d)	S-280	21.5				50	50	
S-102 (d)	S-281	21.5				50	50	
S-103 (d)	S-282	21.5				50	50	
S-104 (d)	S-283	21.5				50	50	
S-105	S-284	21.5				50	50	
S-106	S-285	21.5				50	50	
S-107	S-286	21.5				50	50	
S-108	S-287	21.5				50	50	
S-109	S-288	21.5				50	50	
S-110	S-289	21.5				50	50	
S-111	S-290	21.5				50	50	
S-112	S-291	21.5				50	50	
S-113	S-292	21.5				50	50	
S-114	S-293	21.5				50	50	
S-115	S-294	21.5				50	50	
S-116	S-295	21.5				50	50	
S-117	S-296	21.5	5	Glyceryl succinate	1.0	50	50	
S-118	S-297	21.5	5	Glyceryl succinate	1.0	50	50	
S-119	S-298	21.5	5	Glyceryl succinate	1.0	50	50	
S-120	S-299	21.5	5	Glyceryl succinate	1.0	50	50	
S-121	S-300	21.5	5	Glyceryl succinate	1.0	50	50	
S-122	S-301	21.5	5	Glyceryl succinate	1.0	50	50	

(a) Polymer precipitated from emulsion by addition of 200 ml of CH_3OH in S-71 through S-77, S-96, S-107 through S-119. In all the other examples no reagent was used to precipitate the polymer from the emulsion; the emulsion was merely stirred with the r-mono slurry of RDX and coagulation occurred.

(b) RDX = 36, picric acid = 99, trinitrotoluene > 100, Composition A > 100, TIE > 100.

(c) RDX = 26, picric acid = 35, trinitrotoluene = 30 to 35, Composition A = 51 to 55, TIE = 67.

(d) Total polymer as noted above, but made up of 91% DEHA and 9% ethyl acrylate.

(e) Total polymer as noted above, but made up of 90% DEHA and 10% ethyl acrylate, 15 CH-39.

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Report No. 621
SPIA/M3Data Questionnaire on
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

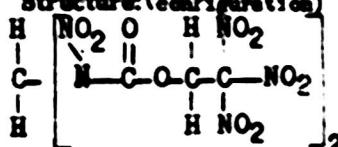
Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound further. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, AFL/JHU, 8431 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND: Methylene N,N'-Dinitro-N,N'

Name bis(trinitroethyl carbamate)

Empirical formula C₇H₆N₂O₂₀

Structure: (configuration)

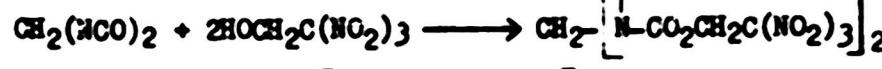


Information submitted by:

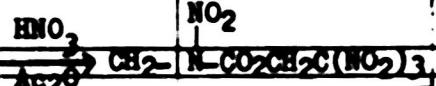
Activity Aerojet Engineering Corporation

Person H. E. Frankel and L. T. Carlton

Date 30 April 1952



Preparation reaction(s):

Impurity from
Melting-Temp.
Curve

1. Quantitative analysis (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen	
Calculated from formula	15.28	1.10	58.16	25.46	
By determination	15.53	1.20	58.25	24.96	1.5 mol%

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)

(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on
separate sheetDiscuss methods used when they vary
from references. Give temperature used.
(See separate sheet if necessary.)

Name of test	Recommended method	
a. Impact Sensitivity	NOL 11401 p.6	2.5-kg weight
b. Thermal Stability	OGRD 3401 p.6	0.3 g at 134.5°C (methyl violet paper)
c. Vacuum Stability	NOL 11401 p.6	18 hr at 100, 120, or 140°C
d. Temperature of Explosion	OGRD 3401 p.6	
e. Temperature of Ignition	NOL 11401 p.6	
f. Thermal Stability at 65.5°C	Picatinny Arsenal No. 11401 0.3 g at 65.5°C (KI-starch	
g. Impact Stability	Bureau of Mines Bull. No. 346, p. 72	paper)
h.		(2-kg weight)

RESULTS OF ABOVE TESTS

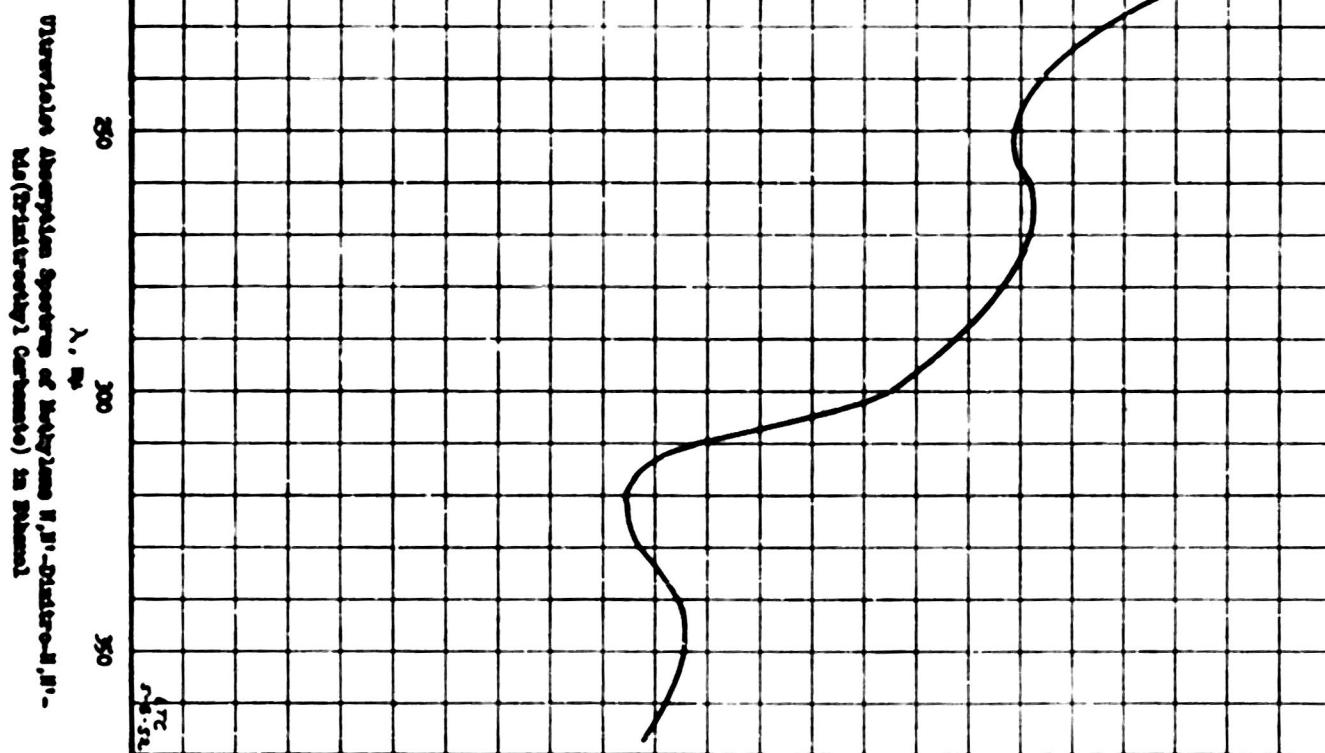
Reference compound (designation-TNT, Tetryl, W.C., etc.)	New Compound test results
a. Tetryl, 32 cm	10.4 cm
b.	Failure in 40 min (2 samples)
c.	1.44 cc/g (100°C); 3.0 cc/g (5 hr at 120°C)
d.	
e.	218°C
f.	Failure in 270, 280 min
g. RDX, 28 cm; PETN, 17 cm	50% Shots at 20 to 25 cm drop
h.	

4. Heat of formation: (AH) + -168 Kg. calories at 25°C., 1 atm. pressure per mol
(Indicate sign)

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By Experiment	By Calculation	Method Description or reference. Separate sheet if necessary.
5. Energy of explosion (Q) (at 25°C. H ₂ O liquid)	cal/gm	
6. Heat of combustion (H _c) (at 25°C. H ₂ O liquid)	1270, 1258 cal/gm	1251
7. Specific impulse (I _{sp}) calc:	lb-sec/lb	
8. Physical form of compound (viscous liquid, crystalline type, etc.)	white prismatic crystals	
9. Simple microscope analysis data: (crystal studies)		
10. Density (Micro method) (MOL)	1.89 gm/cm ³ . (Micro or other method)	gm/cm ³ .
11. Index of refraction (n) (25°C.)		12. Color White
14. pH at 25°C. solvent and concentrations used.	1.6 (Method reference OED 3401 o.4, or OED 9968. Indicate method used, pH indicator used or Beckman pH meter.)	pH indicator used, 1.6. With Beckman pH meter, 0.013M in acetone-water (3.8 vols water)



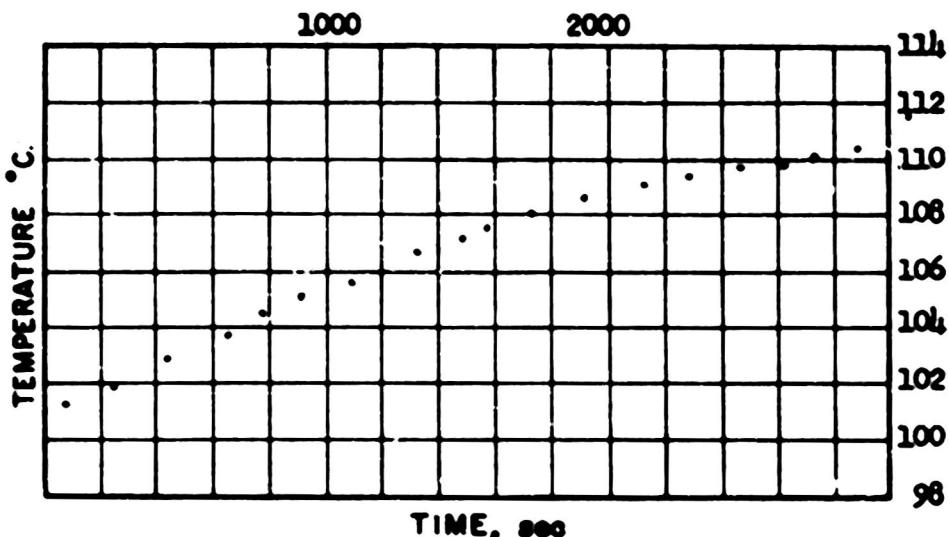
17. Boiling point, or decomposition temperature:
(underline which temperature is reported) °C.
18. Heat of Vaporization: g-cal./gm BTU/lb.
19. Heat of Fusion: 7 (est.) g-cal./gm 13 (est.) BTU/lb.
20. Melting point: 110.9 °C. at 0.0% impurity

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21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)

Apparatus of
Smit, W. M.;
Dissertation,
Amsterdam
(1946)

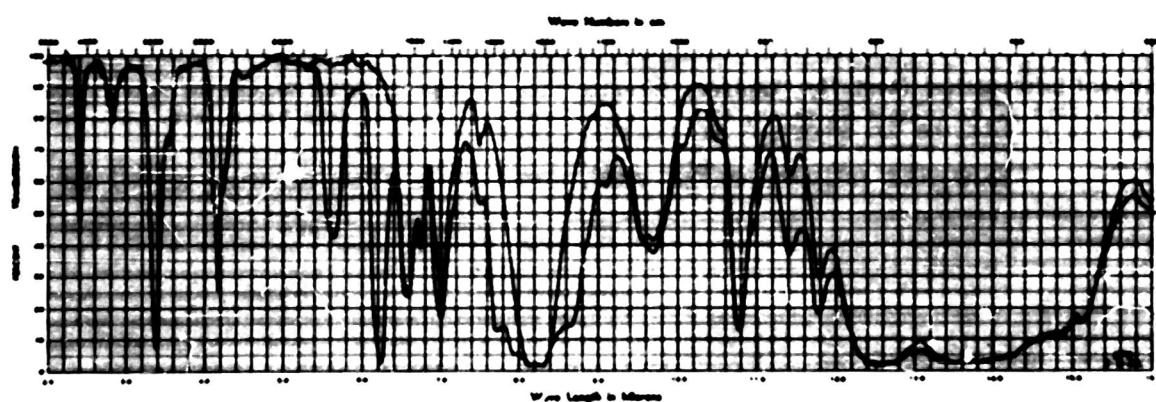


22. Solubility of new compound:

<0.1 g/100 ml H₂O at 25°C. g/100 ml H₂O at °C.
100 g/100 ml cocetone at 25 °C.
2.6 g/100 ml toluene at 25 °C.
(none material used as solvent)

23. Viscosity of the new compound and its solutions:

NEW COMPOUND wt. % in solution	SOLVENT	VISCOOSITY at TEMP. Centipoises	METHOD USED reference
a. <u>100</u>	<u> </u>	<u> </u>	<u>25</u> <u> </u>
b. <u>100</u>	<u> </u>	<u> </u>	<u>25</u> <u> </u>
c. <u>95</u>	<u>D.P. (13.25% w.)</u>	<u>3</u>	<u> </u>
d.			
e.			
f.			



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8 PIA/10

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note QSRD 5745 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber.

25. Compatability with ethyl cellulose: _____

26. Compatability with nitrocellulose: _____

27. Compatability with rubber: _____

28. Compatability with _____: _____

29. Polymerizing properties of the new compound:
(a) By itself _____
(b) In mixtures (with additives) _____
(c) Inhibiting action on polymerization of:
 Thickol _____
 Methacrylate _____
 Other compounds _____

30. Availability
a. Amount now available? _____ Research quantities _____
b. When was available material first prepared? _____
c. Amount prepared at that time? _____
d. Is large production feasible? _____
e. Plant capacity in existence, lbs/day? _____
f. Outline steps for a quantity production method _____

31. Additional information: (toxicity, hazards, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) _____
Stable in storage in refrigerator
Exhibits polymorphism, with metastable form melting at 95 to 96°C

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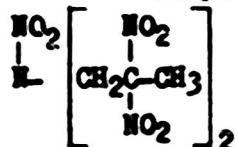
Rate Questionnaire on
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound further. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, AFW/JEW, 8621 Georgia Avenue, Silver Spring, Maryland. An additional information on the same or new compounds occurs, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

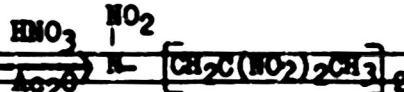
COMPOUND:

Name bis(2,2-Dinitropropyl) nitramineEmpirical formula C₆H₁₀N₂O₁₀

Structure (configuration)



Preparation reaction(s):



Information submitted by:

Activity Aerojet Engineering CorporationPerson H.B. Frankel and L.T. CarltonDate 30 April 1952

1. Quantitative analysis (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	22.09	3.09	49.05	25.17		
By determination	22.52	2.94	48.57	25.17		

2. Burning properties (compared to nitrocellulose, under nitrogen at atmospheric pressure.)

(faster? slower? residue? etc.)

3. Stability and Sensitivity. Plot oxy graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test	Recommended method
a. Impact Sensitivity	NOL CHARTER
b. Thermal Stability	OSRD 3401 p.8
c. Vacuum Stability	NOL CHARTER
d. Temperature of Explosion	OSRD 3401 p.8
e. Temperature of Ignition	NOL CHARTER
f. Thermal Stability at 65.5°C	Picatinny Arsenal No. 1401 0.3 g at 65.5°C (K-Starch)
g. Impact Stability	Bureau of Mines Bull. No. 346, p. 72 (2-kg weight) paper)
h.	

RESULTS OF ABOVE TESTS

Reference compound
(designation-Tetryl, Tetryl, E.C., etc.)

New Compound test results

a. Tetryl, 32 cm	28.5 cm
b.	Failure in 250 min (2)
c. Tetryl, 1.42 cc/g (120°C); 58.0 cc/g (ext. to 110°C)	0.32 cc/g (120°C); 6.15 cc/g (110°C)
d.	236°C
e.	No failure after 5 hr
f.	100 shots at 10 to 15 cm drop
g. HMX 28 cm; PETN 17 cm	
h.	

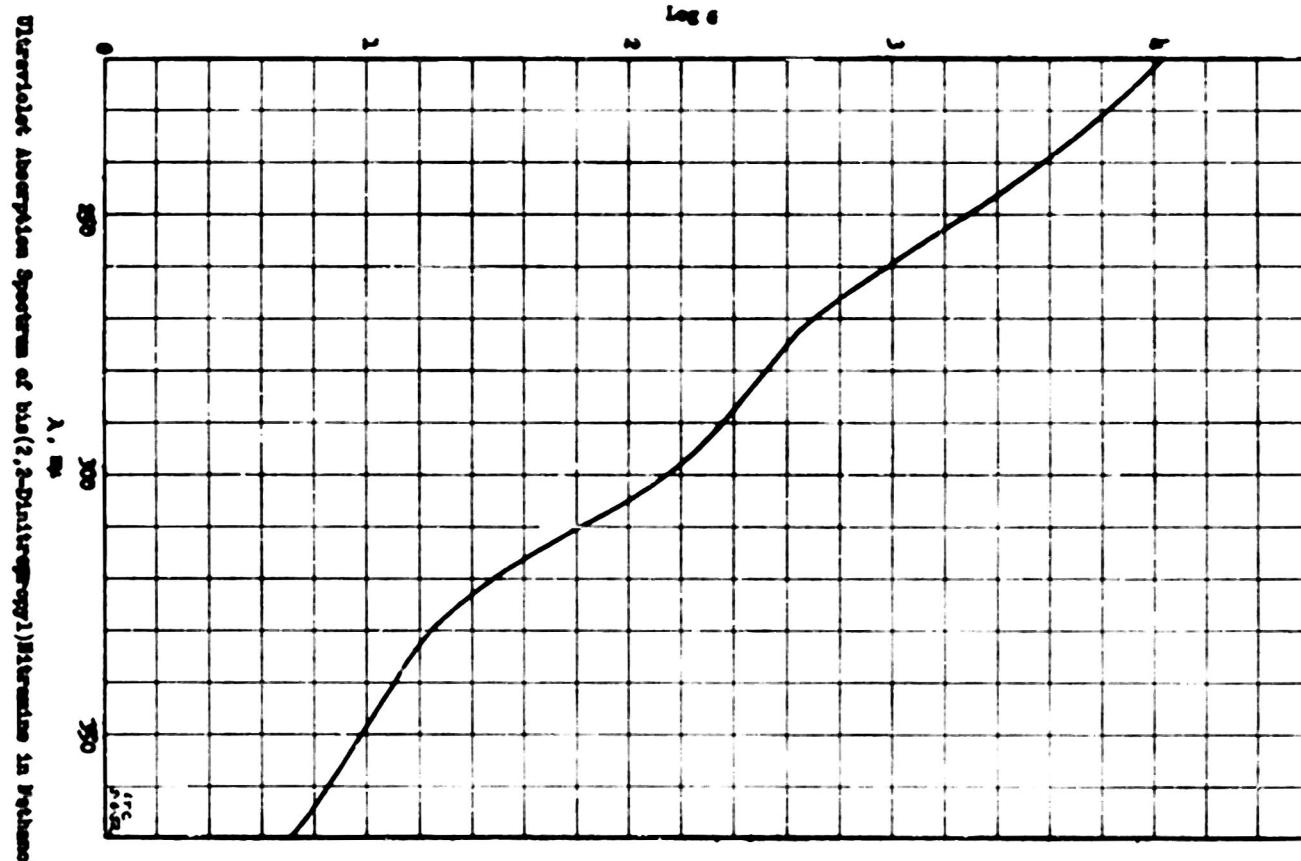
4. Heat of formation: (ΔH_f) \pm -65 (Indicate sign) Kg. calories at 25°C., 1 atm. pressure per mol

(NOTE: Sample tested by NOL was recrystallized before tests)

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	By Experiment	By Calculation	Method Description or reference. Separate sheet if necessary.
5. Energy of explosion (Q)	(at 25°C. H ₂ O liquid) _____	cal/gm _____	
6. Heat of combustion (H _c)	2560, 2597 (at 25°C. H ₂ O liquid) _____	cal/gm 2600	Aerojet Eng. Corp. Report No. 417A
7. Specific impulse (I _{sp}) calc:	_____ lb-sec/lb _____		
8. Physical form of compound (viscous liquid, crystalline type, etc.)	White, tabular crystals		
9. Simple microscope analysis data: (crystal studies)	_____		
10. Density (Macro method) (NOL)	1.73 gm/cm ³ . (Micro or other method) _____	gm/cm ³ .	(Carolina on separate sheet any unique methods you use.)
11. Index of refraction (n _D) 25°C.	_____	12. Color White	13. Odor None
14. pH at 25°C. 7.1	(Method reference QSRD 3401 o.4, or QSRD 5968. Indicate method used, i.e., solvent and concentrations used. pH indicator paper or Beckman pH meter.) With Beckman pH meter, 0.010M in acetone-water (3.8 vol% water)		

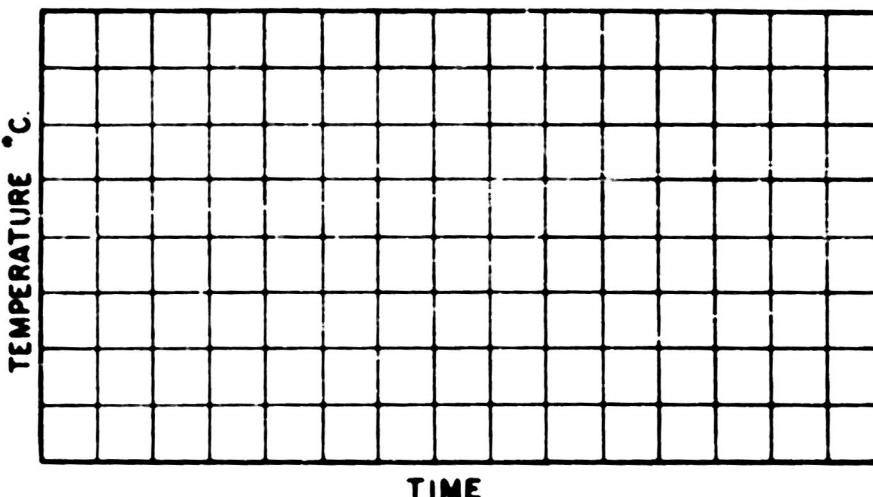


17. Boiling point, or decomposition temperature: _____ °C.
(underline which temperature is reported)
18. Heat of Vaporization: _____ g-cal./gm _____ BTU/lb.
19. Heat of Fusion: _____ g-cal./gm _____ BTU/lb.
20. Melting point: 187 °C.

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21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)



- ## 22. Solubility of new compound:

<0.1 g/100 ml H₂O at 25°C. _____ g/100 ml H₂O at _____ °C.

5.5 g/100 ml acetone
(same material used as solvent) at 25 °C.

<0.1 g/100 ml toluene at 25 °C.
(same material used as solvent)

- ## 29. Viscosity of the new compound and its solutions

NEW COMPOUND wt. % in solution	SOLVENT NAME	NAME in solution	VISCOSITY at TEMP. Centigrade °C.	METHOD USED reference
a. 100		NONE		25
b. 100		NONE		
c. 95	U.T. (13.195 g.)	5		25
d.				
e.				
f.				

24. Ability to plasticize nitrocellulose: Ability to plasticize is to be a general summary of the results of tests you make to note the activity of the compound under study when it is in an intimate mixture with nitrocellulose. For example, make a mixture by thorough extensive mixing and rolling, using 40% by wt. of the new compound and 60% by wt. of the standard N.C. Use as standard N.C. a blend having 13.1% nitrogen and 30-50 poises viscosity determined by the capillary tube method, at 25°C., on a mixture of 10% N.C., 10% ethyl alcohol and 80% acetone, by wt. which has been mixed by 24 hours rolling in a suitable container. Items to consider regarding new compound might include: its solubility, effects on the mixture by age, heat, light, and moisture. Does it separate or crystallize? Does it form bubbles by decomposition? Does the mixture shrink on standing? Does the compound affect flexibility or pliability of the nitrocellulose?

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SPIA/MS

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note 200D 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of oxidation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stock in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 26 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber.

25. Compatibility with ethyl cellulose: _____

_____26. Compatibility with nitrocellulose: _____

_____27. Compatibility with rubber: _____

_____28. Compatibility with _____: _____

_____29. Polymerizing properties of the new compound:
(a) By itself _____
(b) In mixtures (with additives) _____
(c) Inhibiting action on polymerization of:
 Thickol _____
 Methacrylate _____
 Other compounds _____30. Availability
a. Amount now available? **Research quantities**
b. When was available material first prepared? _____
c. Amount prepared at that time? _____
d. Is large production feasible? _____
e. Plant capacity in existence, lbs/day? _____
f. Outline steps for a quantity production method _____

_____31. Additional information: (tendrity, insolubility, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) **Stable in storage in refrigerator**

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SPIA/M3

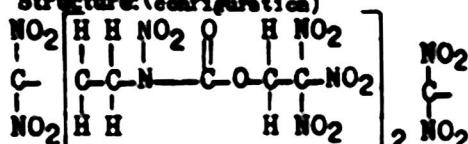
Part Questionnaire on
COMPOUNDS FOR USE AS INGREDIENTS OF PROPELLANTS AND OTHER EXPLOSIVES

Listed below are the characteristics which are believed to be of importance in the study of a compound which may possibly be used as a constituent of solid propellants or other explosives. It is not expected that all this information will be available for every compound. For example, with a compound showing poor stability, it is probably not advisable to investigate that compound further. After placing such information as is available for a compound which you have prepared or tested on one of these forms, send it to SOLID PROPELLANT INFORMATION AGENCY, AF/PAW, 6621 Georgia Avenue, Silver Spring, Maryland. As additional information on the same or new compounds accrues, forward it on a similar form at a later date. The information submitted on these forms will be rewritten and published by SPIA in loose-leaf manual form. These forms may also be used as work or data sheets for your experimental studies. Extra copies are available upon request from SPIA. Suggestions for improvement of these forms are invited. If insufficient space has been provided for any item, attach separate sheets.

COMPOUND: 3,3-Dinitro-1,5-pentane-N,N'-dinitro-N,N'-

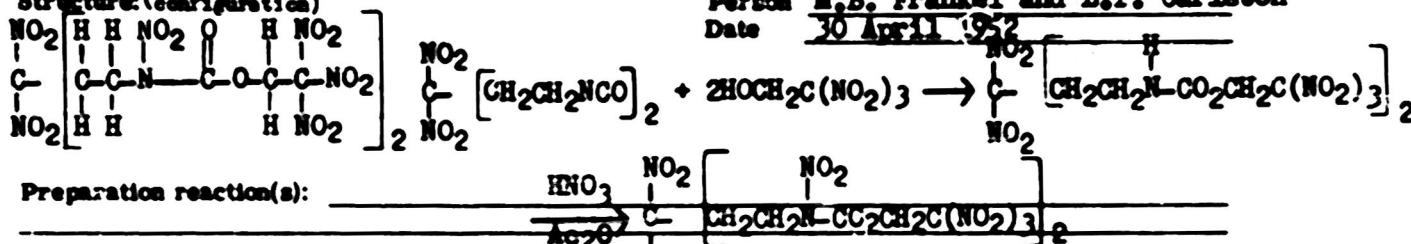
Name bis(trinitrostyryl carbamate)Empirical formula C₁₁H₁₂N₂O₂

Structure (configuration)

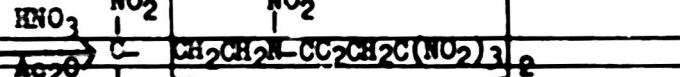


Information submitted by:

Activity Aerojet Engineering Corporation

Person M.B. Frankel and L.T. CarltonDate 30 April 1956

Preparation reaction(s):



1. Quantitative analysis (% by weight)

	Carbon	Hydrogen	Oxygen	Nitrogen		
Calculated from formula	18.97	1.74	55.15	24.14		
By determination	19.19	1.77	55.47	23.87		

2. Burning properties: (compared to nitrocellulose, under nitrogen at atmospheric pressure:)

(faster? slower? residue? etc.)

3. Stability and Sensitivity: Plot any graphs on separate sheet

Discuss methods used when they vary from references. Give temperature used. (Use separate sheet if necessary.)

Name of test

Recommended method

a. Impact Sensitivity	NOL CRIMSON	2.5-kg weight
b. Thermal Stability	OSRD 3401 p.8	0.3 g at 134.5°C (methyl violet paper)
c. Vacuum Stability	NOL CRIMSON	148 hr at 100, 120, or 140°C
d. Temperature of Explosion	OSRD 3401 p.6	
e. Temperature of Ignition	NOL CRIMSON	
f. Thermal Stability at 65.5°C	Picatinny Arsenal No. 1401 0.3 g at 65.5°C (KI-Starch paper)	
g. Impact Stability	Bureau of Mines Bull. No. 346, p. 72 (2-kg weight)	
h.		

RESULTS OF ABOVE TESTS

Reference compound
(designation-TNT, Tetryl, W.C., etc.)

New Compound test results

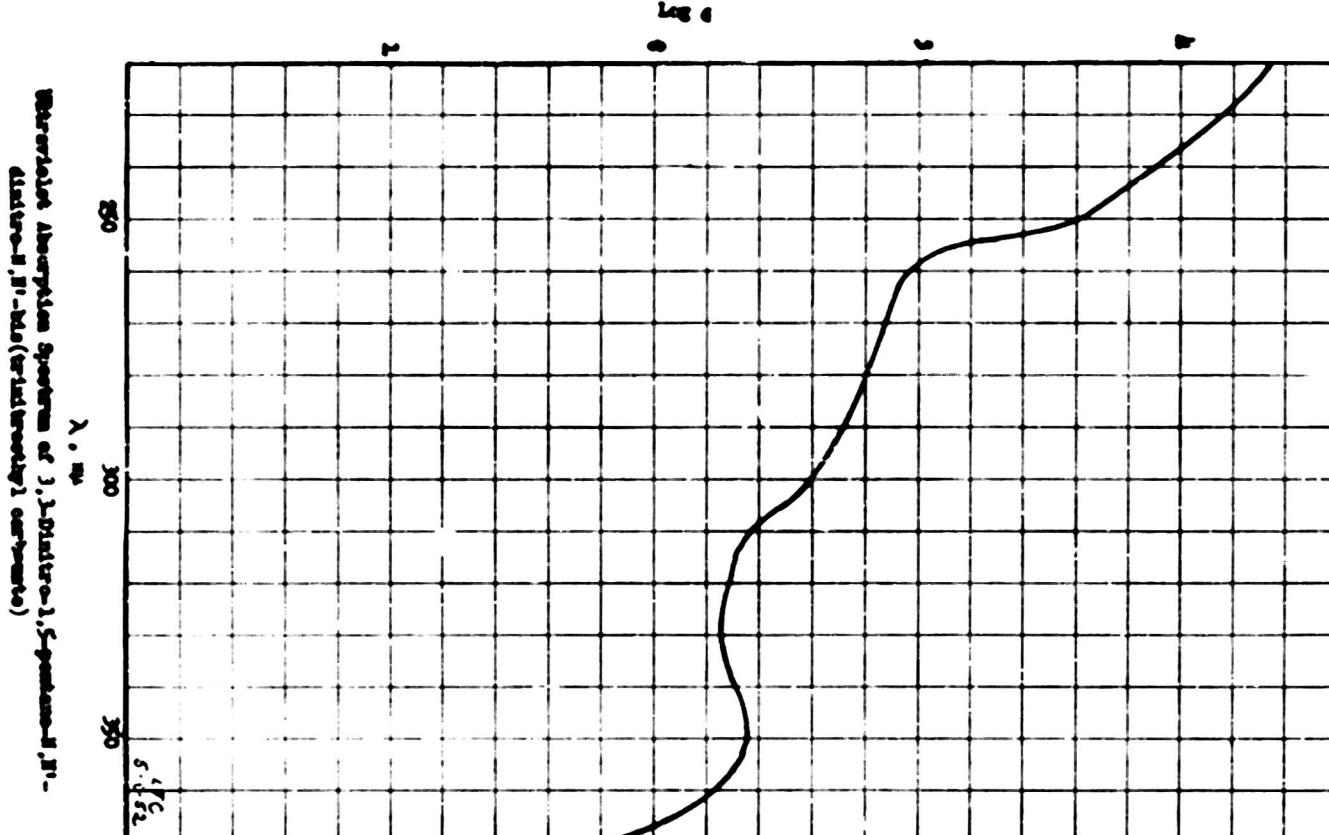
a. Tetryl, 32 cm	12.3 cm
b.	No failure after 5 hr
c. Tetryl, 1.42 cc/g (120°C); 58.0 cc/g (ext. to 110°C)	1.40 cc/g (100°C)
d.	221°C
e.	
f.	No failure after 5 hr
g. RDX, 28 cm; PETN, 17 cm	50% shots at 10 to 15 cm
h.	

4. Heat of formation: (AH) -215 Kg. calories at 25°C., 1 atm. pressure per mol
(Invert. sign)

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By Experiment:	By Calculation:	Method Description or reference. Separate sheet if necessary.
5. Energy of explosion (Q_1) (at 25°C. H ₂ O liquid)	cal/gm	
6. Heat of combustion (H _c) (at 25°C. H ₂ O liquid)	1776, 1758 cal/gm	1784 Aerojet Eng. Corp. Report No. 447A
7. Specific impulse (I _{sp}) calc:	lb-sec/lb	
8. Physical form of compound (viscous liquid, crystalline type, etc.)	Fluffy clumps of fine white, prismatic crystals	
9. Simple microscope analysis data: (crystal studies)		
10. Density (Macro method)	1.76 gm/cm ³ . (Micro or other method) (Indicate on separate sheet any unique methods you use.)	gm/cm ³ .
11. Index of refraction (n _D) (25°C.)	12. Color	White 13. Odor
14. pH at 25°C.	1.8	(Method reference OGRD 3401 o.4, or OGRD 3946. Indicate method used, i.e., solvent and concentrations used, pH indicator paper or Beckman pH meter.) With Beckman pH meter, 0.010M in acetone-water (3.8 vol% water)

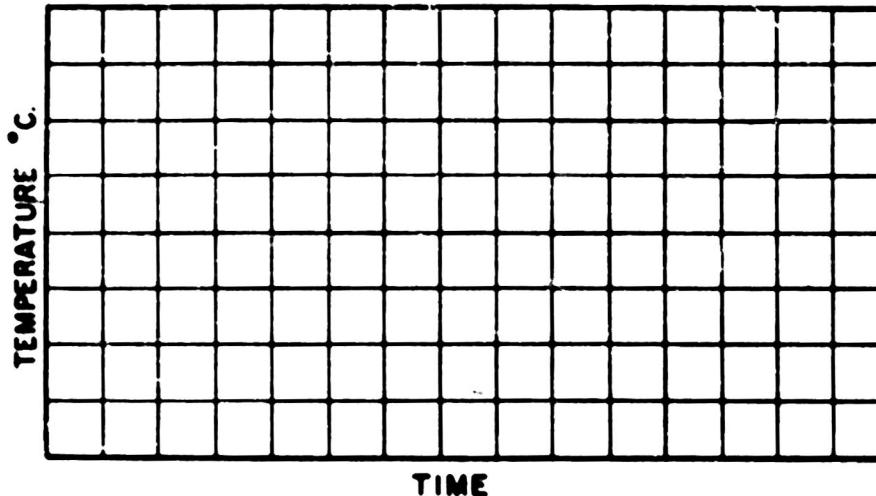


17. Boiling point, or decomposition temperature:
(underline which temperature is reported)
18. Heat of Vaporization: g-cal./gm BTU/lb.
19. Heat of Fusion: g-cal./gm BTU/lb.
20. Melting point: 153-154 °C.

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SFU/MC

21. Freezing point vs. Time Curve: (Please mark the coordinates with scale values that apply to the compound under study.)



- ## 22. Solubility of new compound:

<0.1 g/100 ml HgO at 25°C. _____ g/100 ml HgO at _____ °C.
% g/100 ml acetone at 25 °C.
(name material used as solvent)
0.1 g/100 ml toluene at 25 °C.
(name material used as solvent)

- ### **23. Viscosity of the new compound and its solutions:**

NEW COMPOUND wt. % in solution	SOLVENT		VISCOSEITY at TEMP. Centigrade	METHOD USED reference
a.	water	water	25	
b.	water	water	25	
c.	water (0.1% w/v.)	water	25	
d.				
e.				
f.				

- 24. Ability to plasticize nitrocellulose:** Ability to plasticize is to be a general summary of the results of tests you make to note the activity of the compound under study when it is in an intimate mixture with nitrocellulose. For example, make a mixture by thorough extensive mixing and rolling, using 40% by wt. of the new compound and 60% by wt. of the standard N.C. Use as standard N.C. a blend having 13.15% nitrogen and 30-50 poise viscosity determined by the capillary tube method, at 25°C., on a mixture of 10% N.C., 10% ethyl alcohol and 80% acetone, by wt. which has been mixed by 24 hours rolling in a suitable container. Items to consider regarding new compound might include: its solubility, effects on the mixture by age, heat, light, and moisture. Does it separate or crystallize? Does it form bubbles by decomposition? Does the mixture shrink on standing? Does the compound affect flexibility or pliability of the nitrocellulose?

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SPLA/603

Under compatibility we are considering the ability of two compounds to be in intimate contact (Note OMD 5758 p. 21-22) over a long period of time without adverse effects on either the chemical or physical properties of either material. These tests will probably be of varied extent. They might be some of the following: (a) Standard stability tests. (b) Simple observations of exudation or separation at ambient or accelerated temperature. (c) Prepare thin sheets (.025" thick, 1" square) of the plasticized material. Separate the sheets with strips of cigarette paper or carbon paper and compress the stack in a "C" clamp. After several days note the oily collection on the paper. Please give reference to or describe procedure used. Item 28 is to indicate results when the compound is in contact with some material other than ethyl cellulose, nitrocellulose or rubber.

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Other compounds _____30. Availability
a. Amount now available? Research quantities
b. When was available material first prepared? _____
c. Amount prepared at that time? _____
d. Is large production feasible? _____
e. Plant capacity in existence, lbs./day? _____
f. Outline steps for a quantity production method

_____31. Additional information: (toxicity, insects, deterioration, oxygen balance, detonation rate, explosive power, ease of hydrolysis by water, etc. List references, reports, data books, etc. that refer to the compound.) Stable in storage in refrigerator

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